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Preparation and antibacterial property of SiO_2–Ag/PES hybrid ultrafiltration membranes

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ABSTRACT

Polyethersulfone (PES) ultrafiltration membranes with antibacterial property were prepared by blending with SiO_2–Ag composites via immersion precipitation phase inversion method. In this study, silica sol was prepared by tetraethoxysilane via hydrolysis and polymerization, then silica was mixed with $AgNO_3$ solution, and silver nanoparticles were deposited on the surface of SiO_2 via reduction reaction. FTIR spectra results showed that silica sol was prepared successfully. SiO_2–Ag composites were characterized by transmission electron microscopy (TEM). The hybrid membranes were characterized by permeation properties testing, scanning electron microscopy (SEM), and antibacterial activity analysis. The permeation properties testing indicated that the modified membranes had higher pure water flux than the pure PES membrane. SEM results showed that the structure of membrane was not obviously affected by addition of SiO_2–Ag composites. The antibacterial effect of the SiO_2–Ag/PES hybrid membrane was assayed with *Escherichia coli* and *Staphylococcus aureus* cultures and evaluated with the viable cell count method, and the antibacterial rates of the hybrid membranes against *E. coli* and *S. aureus* could reach 100%.

Keywords: Silica sol; SiO_2–Ag; PES ultrafiltration membrane; Antibacterial activity

1. Introduction

Membrane technology is a kind of new technology, and it has been considered as a useful tool in separation, concentration, and purification process, because it has high separation efficiency, energy saving, low-space requirement, simplicity of operation, and environment friendly [1,2]. Especially, ultrafiltration technology as a novel and powerful technique has been widely used in the food, in pharmaceutical and biotechnological industries, in the chemical industry, in pure water production, and wastewater treatments [3–5].

Polyethersulfone (PES) is a kind of special engineering plastic, and it has been widely used for preparing ultrafiltration membranes as an especially useful membrane material, because PES membranes display many good characteristics such as excellent temperature, pH, chemical stability as well as excellent mechanical strength [6–8] and it is used widely. However, its inherent hydrophobic property often results in fouling during application. The irreversible adsorption of natural organic matter, such as protein on the membrane surface and micro-organisms adhered to the membrane surface, leads to serious membrane fouling. Membrane fouling reduces productivity, shortens membrane life, alters membrane selectivity, and hinders the application range of ultrafiltration membrane [9,10]. It has been generally acknowledged that increasing membrane surface

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hydrophilicity could effectively reduce membrane fouling. In order to improve the PES membrane resistance toward fouling, it is necessary to modify the surface of PES membrane by physical or chemical methods. Many works have been done to increase the hydrophilicity of PES, such as blending with amphiphilic polymer [11] and inorganic materials, especially nanoparticles has received a lot of attention because of their convenient operation and mild conditions. Sotto et al. [12] had incorporated small amount of nanoparticles into PES membranes, they found that the contact angles decrease with increasing TiO_2 concentration until 0.2 wt.%, and the permeability increased with the addition of increasing concentrations of TiO_2, at concentrations above 0.2 wt.%, the permeability decreased. Maximous et al. [13] discovered that PES ultrafiltration membranes blending with Al_2O_3 nanoparticles as inorganic filler had showed lower flux decline during activated sludge filtration compared to pure polymeric membrane. Other inorganic materials also have been used to modify PES membranes, such as carbon nanotube [14], halloysite nanotubes [15], ZnO [16], and so on. Many researches showed that the incorporation of inorganic nanoparticles in the polymer matrix was contributed to improve the membrane antifouling property [17,18].

Though the membrane surface hydrophilicity could be increased by blending with inorganic materials, the PES membrane resistance toward biofouling is still to be improved. In this study, in order to get a novel PES ultrafiltration membrane which has both organic antifouling and antibacterial properties, PES ultrafiltration membranes were prepared by blending with SiO_2–Ag composites via phase inversion method. TEM were used to characterize the SiO_2–Ag composites. The morphology of the membranes was characterized by SEM, and the permeation properties of the membranes were measured by a cross-flow system. In addition, the antibacterial effect of the SiO_2–Ag/PES hybrid membrane was assayed with *Escherichia coli* and *Staphylococcus aureus* cultures and evaluated with the viable cell count method.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES; Mw = 15,000) was supplied by BASF Company and was dried at 80°C for 12 h prior to use. N,N-Dimethylacetamide (DMAc), Polyvinylpyrrolidone (PVP) and PEG20000 were purchased from Kewei Chemical Reagent Co. (Tianjin, PRC). Tetraethoxysilane (TEOS) was obtained from Luoyang Chemical Reagent factory. PVA30000-70000 was supplied by SIGMA–ALDRICH Company. Anhydrous alcohol, methanol, acetone, and other reagents were gained from Shuangshuang Chemical Co. (Yantai, PRC). The test strains, *E. coli* (8099) and *S. aureus* (ATCC6538), used for this study were provided by College of Public Health of Zhengzhou University. Other regents were all of analytical grade and used without further purification. The water used in all experiments was deionized water.

2.2. Modification of SiO_2

2.2.1. Preparation of the silica sol

In order to get the silica sol, firstly, 20.9 g of TEOS was added into 7.2 g of distilled water, and then 1 mL of 12 mol/L hydrochloric acid was added into the solution slowly. Thereafter, the resulting mixture was stirred continuously for 30 min, and then stalled for 6 h. At last, the silica sol was washed with deionized water for 2–3 times.

2.2.2. Preparation of SiO_2–Ag composites

Silver nanoparticles were loaded on the modified silica sol via reduction reaction. About 6 g of the silica sol was added to the tapered bottle, and then 100 mL of methanol and 1 g of nitric acid silver were added into the tapered bottle, the resulting mixture was stirred for half an hour. About 0.3 g of sodium borohydride was added to the mixture, and then adjusts pH to 8 with 1 mol/L NaOH solution, and then the mixture was stirred for 1 h. At last, the modified silica sol was obtained by centrifugation and washed with water for 4–5 times. Finally, the product was dried in vacuum drying chamber at 60°C.

2.3. Preparation of SiO_2–Ag /PES Ultrafiltration membranes

PES ultrafiltration membranes were prepared through immersion precipitation phase inversion method [19]. To prepare casting solutions, the SiO_2–Ag composites were added into 73.2 g of DMAc at different concentrations (0, 0.03, 0.05, and 0.1 SiO_2–Ag /PES ratios, w/w, respectively) and stirred continuously for half an hour for good dispersion. Then PES (18 wt.%), PVP (8 wt.%), and Acetone (0.8 wt.%) were dissolved in the dope solution by continuous stirring at room temperature for 12 h to obtain a uniform and homogeneous casting suspension.

The casting solution was ultrasonicated to remove air bubbles and was stalled for 24 h. Then the casting solution was cast with casting knife with the thickness

of 0.3 mm onto a glass plate at room temperature. The nascent membrane was evaporated at 25°C for 30 s, and the phase inversion was done in a coagulation bath with water at the temperature of 40°C. Further details of membrane preparation were described elsewhere [20]. After complete coagulation, the membrane was kept in deionized water till used. Need to notice that the deionized water should be replaced every day.

2.4. Characterization of SiO_2

In order to confirm whether silica sol was prepared successfully, FTIR spectra of SiO_2 were performed at 2 cm^{-1} resolution with Thermo Nicolet IR 200 spectroscope (Thermo Nicolet Corporation, USA) using KBr pellets. Typically, 64 scans were signal-averaged to reduce spectral noise. And a FEI Model TECNAI G^2 transmission electron microscope (200 kV acceleration voltages) was used to study the surface shapes of the modified SiO_2.

2.5. Characterization of the membranes surface

To visualize membrane surface characteristics, SEM measurements were performed. The samples of the membranes were firstly frozen in liquid nitrogen, and then fractured. Cross-section and surface of the membranes were sputtered with gold and then transferred to the microscope. The morphology of the cross-section and surface of the membranes were inspected by SEM using a JEOL Model JSM-6700F scanning electron microscope (Tokyo, Japan), and the acceleration voltage is 10 kV.

2.6. Flux and rejection

A cross-flow filtration system was used for analyzing the membrane filtration performance. The prepared membranes were characterized for water flux, PEG20000 solution (500 mg/L; pH 6.0), and PVA30000-70000 solution (500 mg/L; pH 6.0) rejection studies. All filtration experiments were conducted at a constant transmembrane pressure of 100 kPa and a system temperature of 25 ± 2°C. The PEG20000 solution and PVA30000-70000 solution were measured after a total of 50 mL of permeate were collected at the feed volume of 1.98 L/min, respectively. Then the concentration of PEG20000 and PVA30000-70000 were obtained by UV-2450 spectrophotometer (Shimadzu, Japan) at the wavelength 505 nm.

The pure water penetration flux is defined as:

$$J = \frac{V}{A \times t} \tag{1}$$

where V is the volume of the permeate pure water (L), A is the effective area of the membrane (m^2), and t is the permeation time (h). In this experiment, the effective area of the membranes was 22.2 cm^2.

The rejection was calculated as follows:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{2}$$

where C_p and C_f are the permeate and feed concentrations of PEG20000 or PVA30000-70000, respectively.

2.7. Tests of antibacterial activity

The antibacterial activity of the hybrid membranes was assessed by the viable cell count method. In the method, two kinds of different bacteria including *E. coli* and *S. aureus* were used. The detailed operating procedure is as follows.

Firstly, *E. coli* and *S. aureus* were inoculated in 5 mL of Luria–Bertani (LB) liquid nutrient medium, respectively, and oscillated for 12 h in the condition of 37°C and 220 r/min rotational speeds, until the exponential growth phase was reached. Then the PES hybrid membrane and the pure PES membrane (0.03 g) were cut and disinfected by autoclaving for 20 min. At last, the membranes were added into the 5 mL solution inoculated by about 10^6 CFU (colony-forming units)/mL of *E. coli* and *S. aureus*, respectively, which was then incubated at room temperature. At the same condition, a suspension culture without any membrane was used as blank sample. After 24 h, membranes were retrieved and washed by normal saline. The wash solutions were collected and diluted 1,000 times with deionized water. About 0.2 mL of dilution solution was stretched onto LB culture medium and all plates were incubated at 37°C for 24 h. The actual number of cells used for the given experiment was determined by the standard serial dilution method and the numbers of colonies on the plates were determined by the plate count method.

The antibacterial rates were calculated as follows:

$$R\ (\%) = \frac{m - n}{m} \times 100\% \tag{3}$$

where m and n are the numbers of bacterial colonies (cfu) in pure PES membrane and SiO_2–Ag/PES hybrid membranes, respectively.

3. Results and discussion

3.1. Characterization of SiO_2

Fig. 1(a) shows the FTIR spectra of SiO_2. The results show that the IR peaks at 797 cm^{-1} and 457 cm^{-1} are resulted from the symmetrical stretching vibration and the bending vibration of Si–O–Si, 1,079 cm^{-1} is the asymmetrical stretch vibration absorption peak of O–Si–O, the absorption band near 3,429 cm^{-1} is the stretch vibration of O−H, and a Si–OH bending band at 956 cm^{-1}. These peaks indicate that SiO_2 was prepared successfully. In Fig. 1(b), the characteristic absorption peaks of SiO_2 still exist, which illustrates that the deposit of silver nanoparticles have no effect on the structure of SiO_2.

Microstructure of SiO_2 and SiO_2–Ag composites were observed by TEM and the images are shown in Fig. 2. From Fig. 2(b), a large number of small particles on the surface of silica sol were found, which indicated that silver nanoparticles had been successfully loaded onto silica sol.

3.2. Flux and rejection of SiO_2–Ag/PES UF membranes

The cross-flow system was used to measure the filtration properties of membranes at 25℃. Filtration

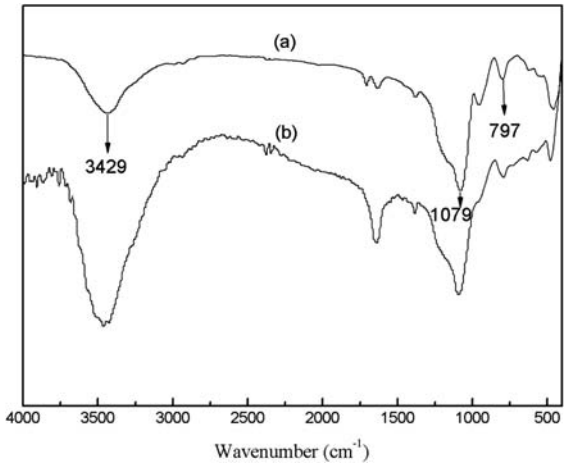

Fig. 1. FTIR spectra of SiO_2 (a) and SiO_2–Ag composites (b).

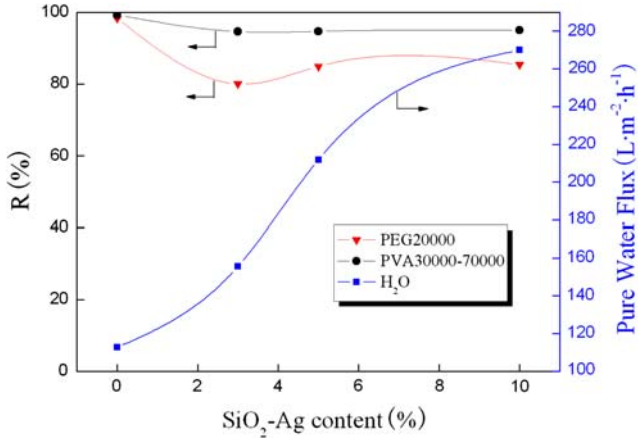

Fig. 3. Effect of the SiO_2–Ag composites contents on the pure water flux and the rejection for PEG20000 and PVA30000-70000.

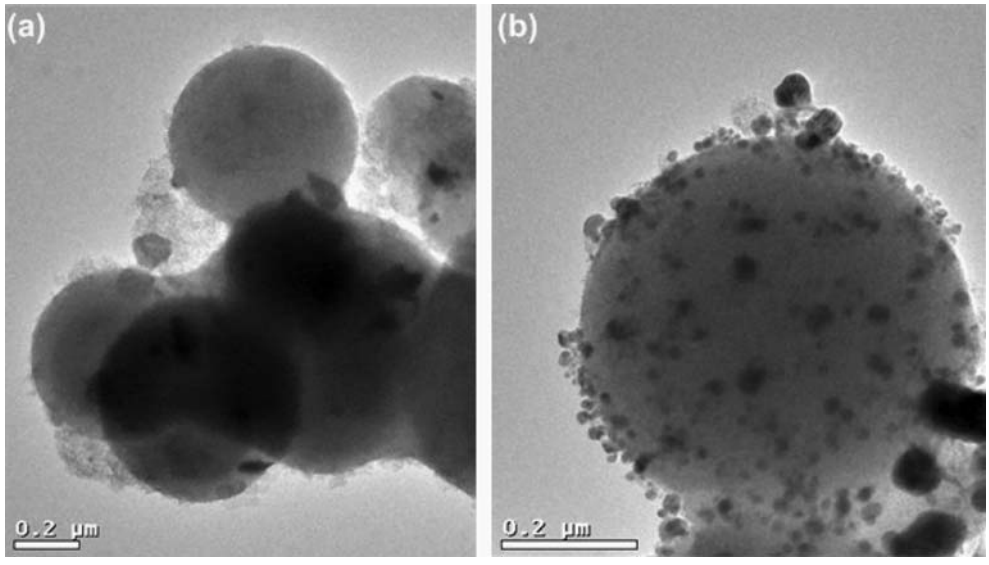

Fig. 2. TEM images of SiO2 (a) and SiO_2–Ag composites (b).

properties of all the prepared membranes are shown in Fig. 3. As is seen that the water flux of all the SiO_2–Ag/PES hybrid membranes were obviously higher than the pure PES membrane. As SiO_2–Ag content increased, the pure water flux of the membranes raised rapidly, especially when the modified SiO_2 content went to 10%, the pure water flux of the membrane reached the maximum at $270\,L\,m^{-}2\,h^{-1}$, which was about 250% higher than that of the pure PES membrane. The PEG20000 and PVA30000-70000 rejection ratios of all the SiO_2–Ag/PES hybrid membranes were both descended. Maybe the addition of SiO_2–Ag composites change the pore size of the membranes, the rejection of the SiO_2–Ag/PES hybrid membranes against PEG20000 decreased obviously. While the rejection of the membranes against PVA30000-70000 was slightly affected by the addition of the modified SiO_2 due to its larger molar mass compared with PEG20000. Thus, it can be seen that the addition of SiO_2–Ag composites slightly change the structure of the membranes. On the whole, the hybrid membranes had a better permeation property than the pure PES membrane.

Hydrophilicity and membrane structure are the two main factors that govern the filtration properties of membranes according to the research of Wu et al. [21]. There are two possible factors that helped to improve the pure water flux of the hybrid

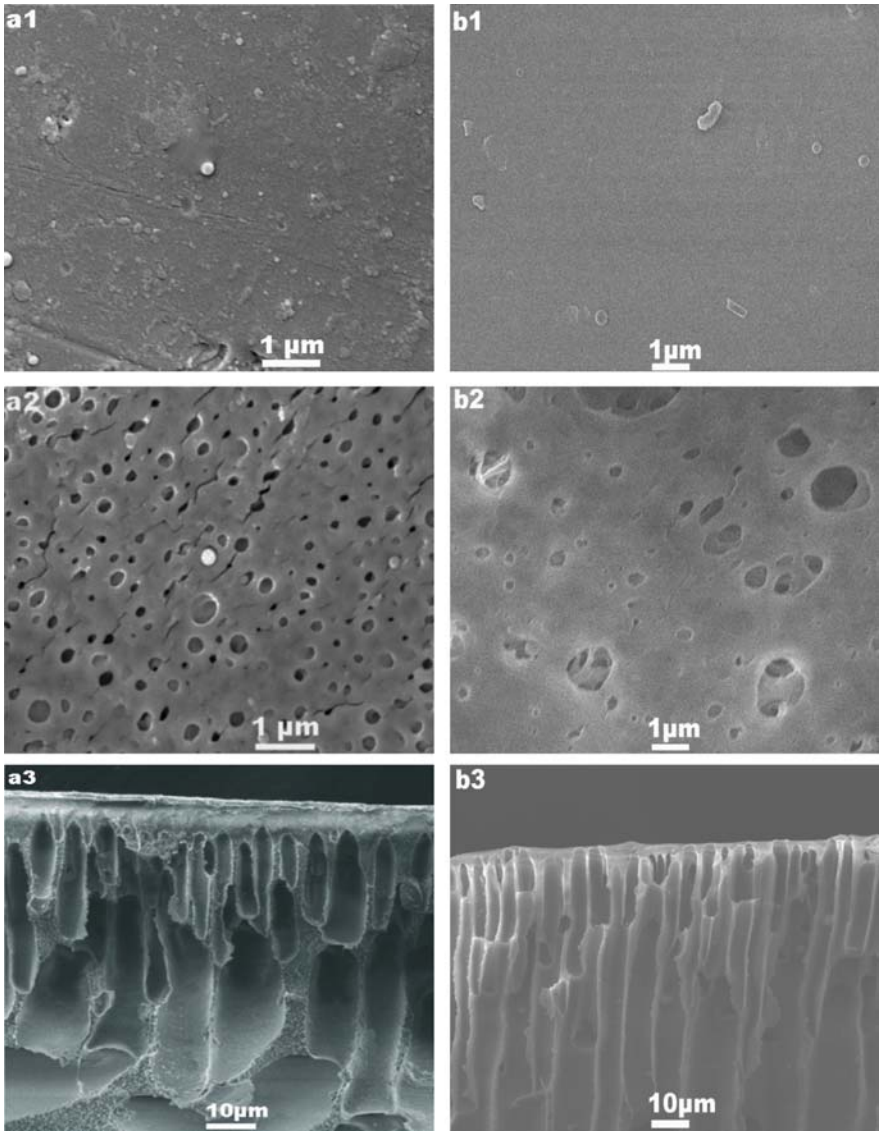

Fig. 4. SEM images of the pure PES membrane (a) and the hybrid membrane (b): 1-top surface; 2-bottom surface; 3-cross-section.

membranes. One is the presence of hydrophilic SiO_2 that improves the hydrophilicity of membranes, which is much beneficial to the water flux. The other is the increase in pore size of the hybrid membranes, which could be seen through a little decrease in the rejection of the membranes. And the role of pore size seems more favorable to improve the water flux according to the work of Razmjou et al. [22]. Consequently, improved hydrophilicity and advantageous membrane structure contribute to higher water flux of SiO_2–Ag/PES hybrid membrane than that of PES membrane.

3.3. Morphology analysis of membranes

SEM was used to observe the surface and cross-sectional morphology of membranes. Fig. 4 shows that there is similar asymmetric structure between pure PES membrane surface and SiO_2–Ag/PES hybrid membrane, such as the typical structure of ultrafiltration membranes, with a top dense layer, a porous sublayer and fully developed macropores at the bottom. On the top surface, there was no obvious difference between the pure PES membrane (a1) and the hybrid membrane (b1), but on the bottom surface, larger pores emerged of the hybrid membrane (b2) compared with pure PES membrane (a2), which maybe favorable to membrane flux.

It is known that the up-layers of the membranes restrict the flux and determine the rejection [23]. The images of cross-section indicate that the addition of SiO_2–Ag results in a decrease in the skin layer thickness compared with pure PES membrane, an increase in the finger-like pore size and an increase in the connectivity of the pores between the sublayer and bottom layer, which relate to increase in membrane flux. On the basis of the frontal analysis, the basic structure of the membrane was not affected greatly by the added SiO_2–Ag, and only a few membrane structure changes appeared a contribution to the increase of membrane flux.

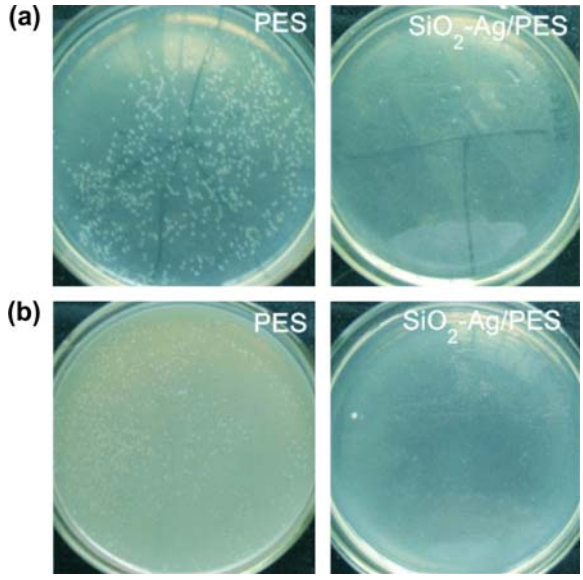

Fig. 5. Photographs showing the bacterial culture plates of (a) *E. coli* and (b) *S. aureus* to PES and SiO_2–Ag/PES NPs.

3.4. Antibacterial effect of the membranes

The antibacterial activities of the SiO_2–Ag/PES hybrid membranes are the main concern in this study. The membrane surface modified by bending with SiO_2 is effective in preventing protein adhesion [24], and Ag nanoparticles are known to exhibit bactericidal effect. Thus, SiO_2–Ag/PES hybrid membranes are expected to exhibit both good antibacterial and antifouling properties.

The pure PES membrane and SiO_2–Ag/PES hybrid membranes were added into the solution inoculated by *E. coli* and *S. aureus*, and the antibacterial activity of the hybrid membrane was evaluated with the viable cell count method [25]. From Fig. 5 and Table 1, compared with pure PES membrane, the antibacterial rates of the hybrid membranes against *E. coli* and *S. aureus* could reach 100%. These results showed that the SiO_2–Ag/PES hybrid membrane had a good antibacterial property.

Table 1
Antibacterial rate of the SiO_2–Ag/PES hybrid membranes against *E. coli* and *S. aureus*

Membranes	*E. coli*		*S. aureus*	
	The numbers of bacterial colonies (cfu)	Antibacterial rates (%)	The numbers of bacterial colonies (cfu)	Antibacterial rates (%)
Pure PES membrane	1,432	–	1,305	–
SiO_2–Ag/PES hybrid membranes	0	100	0	100

4. Conclusion

Novel polyethersulfone hybrid ultrafiltration membranes blending with SiO_2–Ag composites have been successfully prepared via phase inversion. The pure water flux of the SiO_2–Ag/PES hybrid membrane increased greatly compared with the pure PES membrane, and the maximum was $270\,L\,m^{-2}h^{-1}$, which was about 250% higher than that of the pure PES membrane. The SiO_2–Ag/PES hybrid membrane possesses high antibacterial efficiency against both *E. coli* and *S. aureus*, and the antibacterial rates against *E. coli* and *S. aureus* could reach 100%. Therefore, these hybrid membranes have capability of combating with biofouling and can find applications in some areas such as water treatment.

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References

[1] E. Celik, H. Park, H. Choi, H. Choi,Carbon nanotube blended polyethersulfone membranes for fouling control in water treatmentWater Res. 45 (2011) 274–282.
[2] X.G. Chen, Y. Su, F. Shen, Y.H. Wan, Antifouling ultrafiltration membranes made from PAN-b-PEG copolymers: Effect of copolymer composition and PEG chain length, J. Membr. Sci. 384 (2011) 44–51.
[3] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci. 327 (2009) 125–135.
[4] L. Puro, M. Kallioinen, M. Mänttäri, G. Natarajan, D.C. Cameron, M. Nyström, Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters, Desalination 264 (2010) 255–259.
[5] Y.L. Su, C. Li, W. Zhao, Q. Shi, H.J. Wang, Z.Y. Jiang, S.P. Zhu, Modification of polyethersulfone ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the antifouling and permeation properties, J. Membr. Sci. 322 (2008) 171–177.
[6] J. Marchese, M. Ponce, N.A. Ochoa, P. Pradanos, L. Palacio, A. Hernandez, Fouling behavior of polyethersulfone UF membranes made with different PVP, J. Membr. Sci. 211 (2003) 1–11.
[7] Q. Shi, Y.L. Su, S.P. Zhu, C. Li, Y.Y. Zhao, Z.Y. Jiang, A facile method for synthesis of pegylated polyethersulfone and its application in fabrication of antifouling ultrafiltration membrane, J. Membr. Sci. 303 (2007) 204–212.
[8] J.-J. Qin, M.H. Oo, Y. Li, Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, J. Membr. Sci. 247 (2005) 137–142.
[9] M.P. Sun, Y.L. Su, C.X. Mu, Z.Y. Jiang, Improved antifouling property of PES ultrafiltration membranes using additive of silica-PVP nanocomposite, Ind. Eng. Chem. Res. 49 (2010) 790–796.
[10] I.H. Huisman, P. Pradanos, A. Hernandez, The effect of protein and protein-membrane interactions on membrane fouling in ultrafiltration, J. Membr. Sci. 179 (2000) 79–90.
[11] Z. Yi, L.P. Zhu, Y.Y. Xu, Y.F. Zhao, X.T. Ma, B.K. Zhu, Polysulfone-based amphiphilic polymer for hydrophilicity and fouling-resistant modification of polyethersulfone membranes, J. Membr. Sci. 365 (2011) 25–33.
[12] A. Sotto, A. Boromand, R. Zhang, P. Alconero, J.M. Arsuaga, J. Kim, B.V. Bruggen, Effect of nanoparticle aggregation at low concentrations of TiO_2 on the hydrophilicity, morphology and fouling resistance of PES–TiO_2 membranes, J. Colloid Interface Sci. 363 (2011) 540–550.
[13] N. Maximous, G. Nakhla, K. Wong, W. Wan, Optimization of Al_2O_3/PES membranes for wastewater filtration, Sep. Purif. Technol. 73 (2010) 294–301.
[14] E. Celik, L. Liu, H. Choi, Protein fouling behavior of carbon nanotube/ polyethersulfone composite membranes during water filtration, Water Res. 45 (2011) 5287–5294.
[15] J.Y. Zhang, Y.T. Zhang, Y.F. Chen, L. Du, B. Zhang, H.Q. Zhang, J.D. Liu, K.J. Wang, Preparation and characterization of novel polyethersulfone hybrid ultrafiltration membranes bending with modified halloysite nanotubes loaded with silver nanoparticles, Ind. Eng. Chem. Res. 51 (2012) 3081–3090.
[16] S. Balta, A. Sotto, P. Luis, L. Benea, B. Van der Bruggen, J. Kim, A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO, J. Membr. Sci. 389 (2012) 155–161.
[17] J.F. Li, Z.L. Xu, H. Yang, L.Y. Yu, M. Liu, Effect of TiO_2 nanoparticles on the surface morphology and performance of microporous PES membrane, Appl. Surface Sci. 255 (2009) 4725–4732.
[18] N. Maximous, G. Nakhl, W. Wan, K. Wong, Performance of a novel ZrO_2/PES membrane for wastewater filtration, J. Membr. Sci. 352 (2010) 222–230.
[19] T. Matsuura, Synthetic Membranes and Membrane Separation Processes, CRC Press, Boca Raton, FL, 1994.
[20] S.S. Madaeni, A. Rahimpour, Effect of type of solvents and non-solvents on morphology and performance of polysulfone and polyethersulfone ultrafiltration membranes for milk concentration, Polym. Adv. Technol. 16 (2005) 717–724.
[21] H. Wu, B. Tang, P. Wu, Novel ultrafiltration membranes prepared from a multiwalled carbon nanotubes/polymer composite, J. Membr. Sci. 362 (2010) 374–383.
[22] A. Razmjou, J. Mansouri, V. Chen, The effects of mechanical and chemical modification of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes, J. Membr. Sci. 378 (2011) 73–84.
[23] M.F.A. Goosen, S.S. Sablani, H.A. Hinai, S.A. Obeidani, R.A. Belushi, D. Jackson, Fouling of reverse osmosis and ultrafiltration membranes: A critical review, Sep. Sci. Technol. 39 (2004) 2261–2297.
[24] J.N. Shen, H.M. Ruan, L.G. Wu, C.J. Gao, Preparation and characterization of PES–SiO_2 organic-inorganic composite ultrafiltration membrane for raw water pretreatment, Chem. Eng. J. 168 (2011) 1272–1278.
[25] Y.F. Chen, Y.T. Zhang, J.D. Liu, H.Q. Zhang, K.J. Wang, Preparation and antibacterial property of polyethersulfone ultrafiltration hybrid membrane containing halloysite nanotubes loaded with copper ions, Chem. Eng. J. 210 (2012) 298–308.